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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : B01D 53/94, 53/86, F01N 3/20		A1	(11) International Publication Number: WO 99/55446
			(43) International Publication Date: 4 November 1999 (04.11.99)
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(54) Title: PROCESS AND APPARATUS FOR REDUCING THE NITROGEN OXIDE CONTENT IN EXHAUST GASES BY THE CONTROLLED ADDITION OF NH <sub>3</sub>			
<p>Effect of Adsorbed NH<sub>3</sub> on NO<sub>x</sub> Activity of Cu/ZSM5 200ppm NO, 12% O<sub>2</sub>, 4% CO<sub>2</sub>, 200ppm CO</p> <p>Key:          ----- Blank          — Without NH<sub>3</sub>          — With NH<sub>3</sub> Pre-adsorbed       </p>			
(57) Abstract <p>In the reduction of quantities of NO<sub>x</sub> in the exhaust gases of lean burn engines such as diesel engines, using a selective reduction catalyst and a source of ammonia, the present invention improves overall conversion by supplying ammonia or a precursor intermittently so that it is adsorbed and desorbed during the engine operating cycle.</p>			

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## PROCESS AND APPARATUS FOR REDUCING THE NITROGEN OXIDE CONTENT IN EXHAUST GASES BY THE CONTROLLED ADDITION OF NH<sub>3</sub>

5 This invention concerns combatting air pollution from the exhaust gas of a lean burn engine. In particular, it concerns apparatus for, and a method of, reducing the content of nitrogen oxides (NO<sub>x</sub>) in such gas.

Lean burn engines (which have an air-fuel ratio greater than 14.7, generally in the range 19-50) exhibit higher fuel economy and lower hydrocarbon emissions than do stoichiometrically operated engines and are increasing in number. Emissions from diesel  
10 engines are now being regulated by legislation, and whilst it is not too difficult to meet regulations on hydrocarbon or CO emissions, it is difficult to meet regulations on NO<sub>x</sub> emissions. Since exhaust gas from lean burn engines such as diesel engines is high in oxygen content throughout the engine cycle, it is more difficult to reduce NO<sub>x</sub> to nitrogen than in the case of stoichiometrically operated engines. The difficulty is compounded by the  
15 lower gas temperature. Various approaches are being considered to reduce NO<sub>x</sub> under the oxidising conditions. One approach is that of selective catalytic reduction (SCR) with hydrocarbon, but a catalyst of sufficient activity and durability to achieve the required conversion has not been found. Another approach is to adsorb the NO<sub>x</sub> by an adsorbent when the exhaust gas is lean (*ie* when there is a stoichiometric excess of oxygen) and release  
20 and reduce the adsorbed NO<sub>x</sub> when the exhaust gas is rich, the exhaust gas being made rich periodically. During the lean operation, NO is oxidised to NO<sub>2</sub> which can then react readily with the adsorbent surface to form nitrate. This approach, though, is constrained at low temperature by restricted ability to form NO<sub>2</sub> and by adsorbent regeneration and at high temperature by sulphur poisoning. Most adsorbents operate in a certain temperature window  
25 and are deactivated by sulphate formation. The approach of the present invention is that of SCR of NO<sub>x</sub> by NH<sub>3</sub>. This approach has been applied to static diesel engines using a V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> type catalyst.

30 The application of NH<sub>3</sub> SCR technology to the control of NO<sub>x</sub> emission from lean burn vehicles, however, requires a suitable NH<sub>3</sub> supply strategy, especially at low temperature, for various reasons. The engine-out NO<sub>x</sub> varies with temperature, so the amount of NH<sub>3</sub> supplied must be well controlled as a function of the temperature to maintain

the appropriate stoichiometry for the reaction; an insufficient supply of  $\text{NH}_3$  results in inadequate  $\text{NOx}$  reduction, whilst an excess may cause  $\text{NH}_3$  to slip past the catalyst. Whilst at sufficiently high temperature, the catalyst can selectively oxidise that excess  $\text{NH}_3$  to  $\text{N}_2$ , at low temperature, the unreacted  $\text{NH}_3$  will be emitted as such. Even if the proper stoichiometry of  $\text{NH}_3$  is provided, the catalyst may not be sufficiently active at low temperature to react all the  $\text{NH}_3$  with the  $\text{NOx}$ . For example, Figure 1 shows the reaction of  $\text{NH}_3$  with  $\text{NOx}$  over a non-metallised zeolite as a function of temperature at a stoichiometry of 1:1 at an inlet concentration of 200ppm. It can be seen that at temperatures below  $300^\circ\text{C}$  the reduction does not proceed to any significant extent. Furthermore, it has been reported that the presence of excess  $\text{NH}_3$  at low temperature could lead to the formation of  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ . There is also evidence that the presence of excess gas phase  $\text{NH}_3$  can inhibit the  $\text{NH}_3$  SCR reaction over some catalysts at low temperature. Urea is usually the preferred form of storing  $\text{NH}_3$  on a vehicle. Urea is readily available and is stable in water solution. However, it only hydrolyses readily to  $\text{NH}_3$  at temperatures greater than  $150^\circ\text{C}$ , and may not be a suitable source of  $\text{NH}_3$  at low temperature. Exhaust gas temperatures, though, vary over an engine cycle and for the average light duty diesel car a significant fraction of that cycle is at low temperature. Thus, the control of  $\text{NOx}$  at low temperature is a problem.

The present invention provides an improved apparatus and method for reducing the content of  $\text{NOx}$ .

Accordingly, the invention provides apparatus for reducing the content of nitrogen oxides ( $\text{NOx}$ ) in the exhaust gas of a lean burn engine, which apparatus comprises:

- (a) exhaust apparatus through which the exhaust gas flows;
- (b) selective catalytic reduction catalyst in the exhaust apparatus, the catalyst catalysing the reduction of the  $\text{NOx}$  by ammonia to nitrogen and adsorbing and desorbing ammonia during the engine cycle;
- (c) a source of the ammonia;
- (d) supply means to supply the ammonia from the source to the catalyst; and
- (e) means to make the supply of ammonia intermittent during the engine cycle;

whereby the catalyst adsorbs ammonia during its supply and the ammonia which has been adsorbed reacts with the NOx when the ammonia is not supplied.

The invention provides also a method of reducing the content of nitrogen oxides (NOx) in the exhaust gas of a lean burn engine, which method comprises passing the exhaust gas over a selective catalytic reduction catalyst which catalyses the reduction of the NOx by ammonia to nitrogen and which adsorbs and desorbs ammonia during the engine cycle, ammonia being supplied intermittently to the catalyst during the engine cycle, the catalyst adsorbing ammonia during its supply and the ammonia which has been adsorbed reacting with the NOx when the ammonia is not supplied.

We have discovered that ammonia can be adsorbed on a SCR catalyst and thereafter used in the NOx reduction when ammonia is not being supplied. It is an advantage to be able to achieve the NOx reduction while supplying the ammonia intermittently. In particular, the ammonia supply can be halted and yet NOx reduction occur when the temperature of the catalyst is low and supply would have the problems referred to above. The stored ammonia can be used as reductant for NOx over the same catalyst without the presence of gas phase NH<sub>3</sub>.

The ammonia can be supplied without the exhaust gas so that the catalyst adsorbs the ammonia and then the exhaust gas passed over the catalyst for the NOx reduction to occur. Preferably, however, the exhaust gas is passed continuously over the catalyst.

The invention uses adsorption and desorption characteristics of the required catalyst. A higher amount of NH<sub>3</sub> will be adsorbed, and hence be available for subsequent reaction, if adsorption is at a lower temperature than temperatures at which the catalyst adsorbs less NH<sub>3</sub>. Preferably NH<sub>3</sub> is adsorbed at a temperature at which a large amount is adsorbed; the temperature is preferably below that of maximum desorption. The temperature, however, is preferably above that at which any significant formation of ammonium salts occurs. Figure 2 shows the desorption profile from zeolite ZSM5 (non-metallised) of NH<sub>3</sub> which had been pre-adsorbed at 100°C. It can be seen that at say 300°C more NH<sub>3</sub> is retained,

adsorbed, than at say 400°C, and that the temperature of maximum desorption is about 370°C. Bearing in mind that the desorption of NH<sub>3</sub> is endothermic, it can also be seen that if NH<sub>3</sub> were adsorbed at say 300°C and then heated, NH<sub>3</sub> would be desorbed in accordance with the graph so that less would be available for subsequent reaction, while if NH<sub>3</sub> were  
5 adsorbed at the same temperature, 300°C, and cooled, NH<sub>3</sub> would not be desorbed so the adsorbed NH<sub>3</sub> would be available for subsequent reaction. NH<sub>3</sub> stored on the ZSM5 catalyst at 250°C can effectively be used to reduce NOx at a temperature as low as 150°C under exhaust conditions simulating those of a light duty diesel car. Figure 3 shows the NH<sub>3</sub> uptake of ZSM5 catalyst (non-metallised) from a gas mixture containing 4.5% CO<sub>2</sub>, 12%  
10 O<sub>2</sub>, 4.5% H<sub>2</sub>O, 200ppm CO, 100ppm C<sub>3</sub>H<sub>6</sub>, 20ppm SO<sub>2</sub> and 200ppm NH<sub>3</sub> with the balance N<sub>2</sub> at 250°C, and Figure 4 shows the subsequent reaction of that adsorbed NH<sub>3</sub> with NOx at 150°C. It can be seen that significant amounts of NOx are reduced by the adsorbed NH<sub>3</sub> over a period of time and that as the stored NH<sub>3</sub> is being consumed, the reduction reaction declines with time. When the temperature rises in the engine cycle, however, NH<sub>3</sub> can be  
15 supplied again, and hence adsorbed NH<sub>3</sub> replenished. Accordingly, the problem of supplying NH<sub>3</sub> at low temperature can be overcome by halting its supply and using adsorbed NH<sub>3</sub>. The amount of NH<sub>3</sub> adsorbed on a fixed weight of catalyst can be increased by increasing its partial pressure in the gas mixture. For example, Table 1 gives the amount of NH<sub>3</sub> adsorbed by a zeolite at 250°C from a simulated gas mixture of differing NH<sub>3</sub>  
20 concentrations.

**TABLE 1****NH<sub>3</sub> Adsorption as a Function of NH<sub>3</sub> Concentration**

25

NH <sub>3</sub> Concentration (ppm)	Amount NH <sub>3</sub> Adsorbed (mmoles per g)
200	0.63
500	1.22
1000	1.48

30

The means to make the supply of ammonia intermittent during the engine cycle in the present apparatus can be a switch which switches the ammonia supply on and off dependent on the level of NOx conversion occurring over the SCR catalyst. Preferably, however, the means to make the supply of ammonia intermittent comprises a switch to switch on the means to supply the ammonia when the temperature of the catalyst rises above a set level (i) during the engine cycle, and to switch off the means to supply the ammonia when the temperature of the catalyst falls below a set level (ii). The set level (i) is preferably in the range 250-400°C, especially in the range 250-350°C. The set level (ii) is preferably in the range 200-250°C.

The ammonia can be supplied for instance 1-30 times per minute.

The source of ammonia and means to supply it from the source to the catalyst can be conventional. Compounds of ammonia as a solid or a solution in water are preferred. The compounds are preferably urea or ammonium carbamate. The means to supply the ammonia from the source to the catalyst can be a pipe through which it is injected into the exhaust gas up-stream of the catalyst. Thus, the present invention can be employed to provide a method of promoting the conversion of NOx under oxidising conditions in an exhaust fitted with a means of injecting NH<sub>3</sub> and a catalyst which adsorbs NH<sub>3</sub> during parts of the engine cycle in which the exhaust gas is sufficiently warmed for the hydrolysis of NH<sub>3</sub> precursor and injection of ammonia and ammonia is adsorbed by the catalyst for use as reductant for NOx during parts of the engine cycle in which the exhaust gas is cooler, without the need for the continuous injection of NH<sub>3</sub> into the exhaust gas.

It can be seen that the invention provides an exhaust system for an engine operating generally under lean conditions, which exhibits a higher exhaust gas temperature and a lower exhaust gas temperature, the lower exhaust gas temperature being inadequate for the effective hydrolysis of NH<sub>3</sub> precursor and injection of NH<sub>3</sub> (generally a temperature below 200°C), and an NH<sub>3</sub> SCR catalyst arranged and constructed so that during the higher exhaust gas temperature parts of the engine cycle the catalyst adsorbs NH<sub>3</sub> and during the lower

exhaust gas temperature parts of the engine cycle the adsorbed  $\text{NH}_3$  is used as reductant for  $\text{NO}_x$ .

The catalyst can be any which has the required characteristics of the present catalyst.

5 The same material can both selectively catalyse the reduction and also adsorb and desorb the ammonia, and this is preferred. However, different materials in the catalyst can perform the two functions, one material catalysing and one material adsorbing and desorbing. When different materials are employed, they can be physically separate or, preferably, in admixture one with another. A zeolite can perform both functions or a zeolite can be employed which

10 performs one function together with a different material, which may or may not be a zeolite, which performs the other function. The catalyst preferably comprises a zeolite. The zeolite can be metallised or non-metallised, and can have various silica-to-alumina ratios. Examples are metallised or non-metallised ZSM5, mordenite,  $\gamma$  zeolite and  $\beta$  zeolite. Preferred is ZSM5 or ion-exchanged or metal impregnated ZSM5 such as Cu/ZSM5. It may

15 be desirable that the zeolite contains metal, especially Cu, Ce, Fe or Pt; this can improve the low temperature SCR activity. The zeolite can contain for instance 1-10% of metal by weight. The catalyst should have an appropriate structure, for instance in terms of pore size or surface acid sites, to trap and release  $\text{NH}_3$ .

20 The catalyst is preferably carried out on a support substrate, in particular a honeycomb monolith of the flow-through type. The monolith can be metal or ceramic. The substrate can be conventional.

Nitrogen oxide (NO) is usually the most abundant nitrogen oxide in an engine exhaust

25 stream, but at lower temperatures the reaction of the adsorbed  $\text{NH}_3$  on a zeolite catalyst occurs more readily with  $\text{NO}_2$  than with NO. Accordingly it is often desirably to oxidise NO to  $\text{NO}_2$  up-stream of the SCR catalyst, particularly at low temperature.

The present engine can be a diesel or petrol (gasoline) engine. The diesel engine can

30 be a light duty or heavy duty diesel engine. The engine is preferably that of a vehicle.



The invention is illustrated by the accompanying drawings, which are graphs in which:

- Figure 1 shows NO<sub>x</sub> and NH<sub>3</sub> concentrations in simulated exhaust gas against temperature after treatment by zeolite ZSM5, the NH<sub>3</sub> being supplied continuously;
- 5 Figure 2 shows the temperature programmed desorption (TPD) of NH<sub>3</sub> from ZSM5 which had been pre-adsorbed at 100°C, the graph showing, in arbitrary units, the concentration of ammonia in the gas against temperature;
- Figure 3 shows the NH<sub>3</sub> concentration in a full simulated exhaust gas mixture containing 4.5% CO<sub>2</sub>, 12% O<sub>2</sub>, 4.5% H<sub>2</sub>O, 200ppm CO, 100ppm C<sub>3</sub>H<sub>6</sub>, 20ppm SO<sub>2</sub> and 200ppm NH<sub>3</sub> with the balance N<sub>2</sub> after passage over ZSM5 at 250°C against time, and hence shows the NH<sub>3</sub> uptake by the zeolite;
- 10 Figure 4 shows the NO<sub>x</sub> concentration remaining in simulated exhaust gas after passage over the zeolite containing adsorbed NH<sub>3</sub> resulting from the adsorption shown in Figure 3 against time;
- 15 Figure 5 shows the NO<sub>x</sub> concentration remaining in simulated exhaust gas containing 200ppm NO, 200ppm CO, 12% O<sub>2</sub> and 14% CO<sub>2</sub> with the balance N<sub>2</sub> after passage over ZSM5 with and without pre-adsorption of NH<sub>3</sub> against temperature;
- Figure 6 shows the corresponding effect to that shown in Figure 5 of successive cycles of the NH<sub>3</sub> pre-adsorption followed by subjection to the simulated exhaust gas;
- 20 Figure 7 corresponds to Figure 5 but with the simulated exhaust gas containing also hydrocarbon;
- Figure 8 corresponds to Figure 7 but with the simulated exhaust gas containing also H<sub>2</sub>O and SO<sub>2</sub>;
- Figure 9 corresponds to Figure 5 but with the simulated exhaust gas containing NO<sub>2</sub> instead of NO;
- 25 Figure 10 corresponds to Figure 9 but with the simulated exhaust gas containing also hydrocarbon;
- Figure 11 corresponds to Figure 10 but with the simulated exhaust gas containing also H<sub>2</sub>O and SO<sub>2</sub>;
- 30 Figure 12 shows NO<sub>x</sub> concentration and temperature against time during part of an engine cycle;

Figure 13 corresponds to Figure 12 but shows the effect of intermittent supply of  $\text{NH}_3$ ;

Figure 14 shows the  $\text{NO}_x$  concentration remaining in simulated exhaust gas after passage over Cu/ZSM5 with and without pre-adsorption of  $\text{NH}_3$  against temperature; and

Figure 15 shows the  $\text{NO}_x$  concentration remaining in simulated exhaust gas which is that used in relation to Figure 14 but containing also hydrocarbon,  $\text{H}_2\text{O}$  and  $\text{SO}_2$ , after passage over Cu/ZSM5 with pre-adsorption of  $\text{NH}_3$  against temperature.

Figures 1-4 are discussed further hereinbefore, and Figures 5-15 hereinafter.

The invention is illustrated also by the following Examples.

#### **EXAMPLE 1**

##### **Reaction of NO With Pre-adsorbed $\text{NH}_3$ Over Non-metallised ZSM5**

This Example shows the effect of pre-adsorbing  $\text{NH}_3$  at  $250^\circ\text{C}$  on the conversion of  $\text{NO}_x$  over a non-metallised zeolite in a simple gas mixture containing  $\text{NO}_x$ , CO,  $\text{CO}_2$  and  $\text{O}_2$  during a light-off test from room temperature to  $400^\circ\text{C}$ . The gas stream containing NO (200ppm), CO (200ppm),  $\text{O}_2$  (12%),  $\text{CO}_2$  (14%) with the balance  $\text{N}_2$  at a flow rate of 2 litres per minute was first passed over the non-metallised zeolite (0.4g) from room temperature to  $400^\circ\text{C}$  at a heating rate of  $50^\circ\text{C}$  per minute and the  $\text{NO}_x$  at the outlet measured. In a subsequent experiment, the catalyst temperature was first raised to  $250^\circ\text{C}$  and 200ppm  $\text{NH}_3$  was added to the gas stream, the zeolite was exposed to that stream for 5 minutes and then the  $\text{NH}_3$  switched off, and the catalyst was cooled to room temperature and the rapid light-off repeated. Figure 5 shows the outlet  $\text{NO}_x$  concentration for these experiments. It can be seen that in the case where  $\text{NH}_3$  was not pre-adsorbed over the catalyst, some of the  $\text{NO}_x$  is adsorbed on the zeolite at low temperature and is then subsequently released between  $150^\circ\text{C}$  and  $350^\circ\text{C}$ , but that when  $\text{NH}_3$  was pre-adsorbed on the zeolite, the zeolite did not adsorb a significant amount of  $\text{NO}_x$  at low temperature. Furthermore, it can be seen that a decrease in the outlet  $\text{NO}_x$  concentration occurs from  $150^\circ\text{C}$  to  $450^\circ\text{C}$  due to the reaction of the  $\text{NO}_x$  with the pre-adsorbed  $\text{NH}_3$ . This effect of reacting the adsorbed  $\text{NH}_3$  with the

NOx can be repeated over successive cycles with NH<sub>3</sub> injection at 250°C between each cycle, as is shown in Figure 6.

We have also shown that even in the presence of other gaseous components such as hydrocarbon, H<sub>2</sub>O and SO<sub>2</sub>, the adsorption of NH<sub>3</sub> will readily occur on the zeolite and can be used to reduce NOx. For example, Figure 7 shows the effect of adding 200ppm C<sub>3</sub>H<sub>6</sub> to the gas mixture in similar tests to those described above and Figure 8 shows the effect of further addition of H<sub>2</sub>O (10%) and SO<sub>2</sub> (20ppm). It can be seen that in both cases NOx was reduced by the adsorbed NH<sub>3</sub>.

## EXAMPLE 2

### Reaction of NO<sub>2</sub> with Pre-adsorbed NH<sub>3</sub> Over Non-metallised ZSM5

The selective catalytic reduction of NOx by NH<sub>3</sub> under oxidising conditions proceeds more rapidly at low temperature if NO<sub>2</sub> instead of NO is present. The present Example shows that NH<sub>3</sub> pre-adsorbed on a zeolite catalyst can be used to reduce NO<sub>2</sub> even at a temperature as low as 100°C. This was demonstrated by rapid light-off tests analogous to that described above in Example 1. In the first experiment, a simple gas mixture containing NO<sub>2</sub> (200ppm), CO (200ppm), O<sub>2</sub> (12%), CO<sub>2</sub> (14%) with the balance N<sub>2</sub> at a flow rate of 2 litres per minute was passed over the non-metallised zeolite (0.4g) from room temperature to 400°C at a heating rate of 50°C per minute. In a subsequent experiment, the catalyst temperature was first raised to 250°C and 200ppm NH<sub>3</sub> was added to the gas stream, the zeolite was exposed to that stream for 5 minutes and then the NH<sub>3</sub> was switched off, and the catalyst was cooled to room temperature and the rapid light-off repeated. Figure 9 shows the outlet NOx concentration from these experiments. It can be seen that in the absence of pre-adsorbed NH<sub>3</sub>, NO<sub>2</sub> is adsorbed at low temperature over the zeolite and is released between 100°C and 300°C, but when NH<sub>3</sub> was pre-adsorbed on the catalyst, significant NOx reduction is shown over the entire temperature window up to 400°C.

We have also shown that even in the presence of hydrocarbon, H<sub>2</sub>O and SO<sub>2</sub> adsorbed NH<sub>3</sub> will readily react with NO<sub>2</sub>. Figure 10 shows the effect of adding C<sub>3</sub>H<sub>6</sub> on the reaction

of pre-adsorbed  $\text{NH}_3$  with NOx, and Figure 11 demonstrates the effect with addition of  $\text{H}_2\text{O}$  and  $\text{SO}_2$ .

### **EXAMPLE 3**

#### **Reaction of $\text{NO}_2$ With Pre-adsorbed $\text{NH}_3$ Over Non-metallised ZSM5 in Cycle Test**

In most cases, exhaust gas temperature varies during an engine cycle and for a significant fraction of that time the temperature can be low. We have shown that by injecting  $\text{NH}_3$  over a set temperature during the cycle, the adsorbed  $\text{NH}_3$  can subsequently be utilised in reducing NOx at both low and high temperature. In the experiment, exhaust gas containing  $\text{CO}_2$  (14%),  $\text{O}_2$  (12%),  $\text{H}_2\text{O}$  (10%), CO (200ppm),  $\text{C}_3\text{H}_6$  (200ppm),  $\text{SO}_2$  (20ppm) and  $\text{NO}_2$  (200ppm) was cycled between 150°C and 350°C with a dwell of approximately 5 minutes at 250°C during the cooling-down part of the cycle. The  $\text{NH}_3$  injection was switched on when the temperature was at 350°C and switched off when the temperature fell to 250°C. Figure 12 shows the outlet NOx concentration and the temperature against time without any  $\text{NH}_3$  injection, and Figure 13 shows the effect of the cycling with the intermittent injection of  $\text{NH}_3$ . In both Figures, the ordinate scale gives the degrees C for the temperature graph and the parts per million (ppm) for the NOx graph.

### **EXAMPLE 4**

#### **Reaction of NO With Pre-adsorbed $\text{NH}_3$ Over Cu/ZSM5**

This Example shows the effect of pre-adsorbing  $\text{NH}_3$  at 250°C on the conversion of NOx over a Cu-impregnated ZSM5 (containing 5% copper by weight) in a simple gas mixture containing NOx, CO,  $\text{CO}_2$  and  $\text{O}_2$  during a light-off test from room temperature to 400°C. The gas stream containing NO (200ppm), CO (200ppm),  $\text{O}_2$  (12%),  $\text{CO}_2$  (14%) with the balance  $\text{N}_2$  at a flow rate of 2 litres per minute was first passed over the Cu/ZSM5 (0.4g) from room temperature to 400°C at a heating rate of 50°C per minute and the NOx at the outlet measured. In a subsequent experiment, the catalyst temperature was first raised to 250°C and 200ppm  $\text{NH}_3$  was added to the gas stream, the Cu/ZSM5 was exposed to that stream for 5 minutes and then the  $\text{NH}_3$  was switched off, the catalyst was cooled to room

temperature rapidly and the light-off repeated. Figure 14 shows the outlet NOx concentration for these experiments. It can be seen that in the case where NH<sub>3</sub> was not pre-adsorbed on the catalyst, some of the NOx is adsorbed on the zeolite at low temperature, and is then subsequently released at higher temperature, but the pre-adsorption of NH<sub>3</sub> at 250°C suppresses the amount of NOx adsorbed at low temperature, with significant NOx reduction by the pre-adsorbed NH<sub>3</sub> at temperatures greater than 125°C.

Similarly, even in the presence of other gaseous components such as hydrocarbon, H<sub>2</sub>O and SO<sub>2</sub> the adsorption of NH<sub>3</sub> will occur readily over the Cu/ZSM5 and can be used to reduce NOx. For example, Figure 15 shows the effect of pre-adsorbing NH<sub>3</sub> on the Cu/ZSM5 at 250°C from a gas mixture containing NO, H<sub>2</sub>O, CO<sub>2</sub>, CO, C<sub>3</sub>H<sub>6</sub>, SO<sub>2</sub> and O<sub>2</sub> and the reduction of NOx by the adsorbed NH<sub>3</sub> during a light-off test.

**CLAIMS**

1. Apparatus for reducing the content of nitrogen oxides (NO<sub>x</sub>) in the exhaust gas of a lean burn engine, which apparatus comprises:
- 5 (a) exhaust apparatus through which the exhaust gas flows;
- (b) selective catalytic reduction catalyst in the exhaust apparatus, the catalyst catalysing the reduction of the NO<sub>x</sub> by ammonia to nitrogen and adsorbing and desorbing ammonia during the engine cycle;
- (c) a source of the ammonia;
- 10 (d) supply means to supply the ammonia from the source to the catalyst; and
- (e) means to make the supply of ammonia intermittent during the engine cycle;
- whereby the catalyst adsorbs ammonia during its supply and the ammonia which has been adsorbed reacts with the NO<sub>x</sub> when the ammonia is not supplied.
- 15 2. Apparatus according to claim 1 adapted to pass the exhaust gas continuously over the catalyst.
3. Apparatus according to claim 1 or 2 wherein the means to make the supply of ammonia intermittent during the engine cycle, (e), comprises a switch to switch on the supply means, (d), when the temperature of the catalyst rises above a set level, (i), during the engine cycle, and to switch off the supply means, (d), when the temperature of the catalyst falls below a set level, (ii).
- 20 4. Apparatus according to claim 3 wherein the set level (i) is in the range 250-400°C and the set level (ii) is in the range 200-250°C.
- 25 5. Apparatus according to any one of claims 1-4 wherein the catalyst comprises the same material which both selectively catalyses the reduction and also adsorbs and desorbs the ammonia.
- 30

6. Apparatus according to any one of the preceding claims wherein the catalyst comprises a zeolite.
7. Apparatus according to claim 6 wherein the zeolite is non-metallised.
- 5 8. Apparatus according to claim 7 wherein the zeolite is ZSM5.
9. Apparatus according to claim 6 wherein the zeolite contains metal.
- 10 10. Apparatus according to claim 9 wherein the zeolite is Cu/ZSM5.
11. A method of reducing the content of nitrogen oxides (NOx) in the exhaust gas of a lean burn engine, which method comprises passing the exhaust gas over a selective catalytic reduction catalyst which catalyses the reduction of the NOx by ammonia to nitrogen and  
15 which adsorbs and desorbs ammonia during the engine cycle, ammonia being supplied intermittently to the catalyst during the engine cycle, the catalyst adsorbing ammonia during its supply and the ammonia which has been adsorbed reacting with the NOx when the ammonia is not supplied.

Fig.1.  $\text{NO}_x$  and  $\text{NH}_3$  conversion on ZSM5 in dynamic conditions  
0.4 g ZEOLITE 2 Litres per minute and 200ppm  $\text{NO}_x$

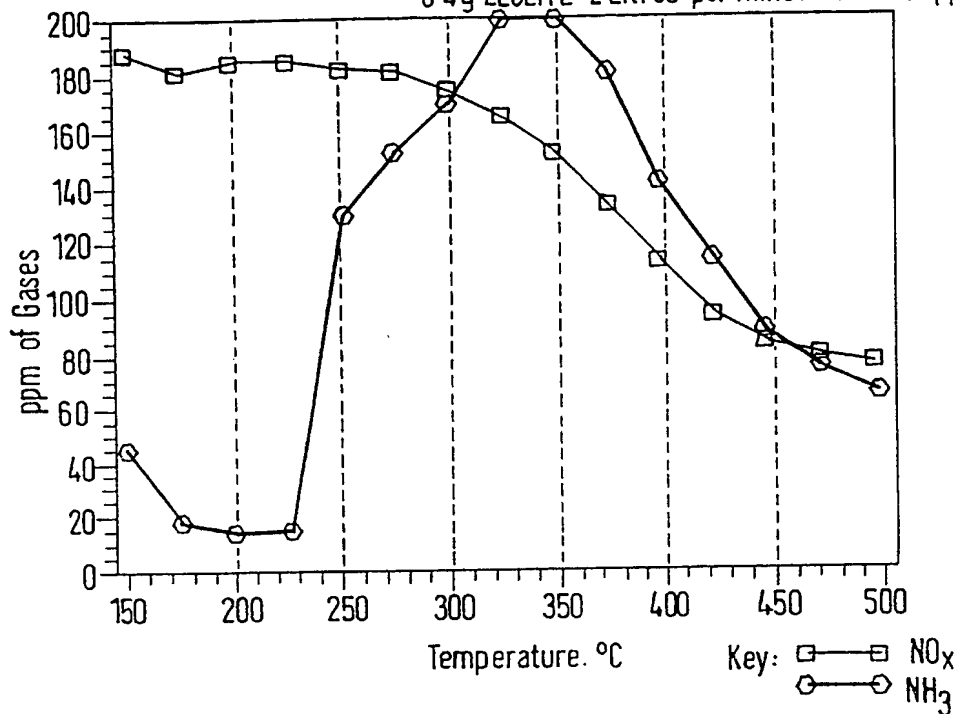
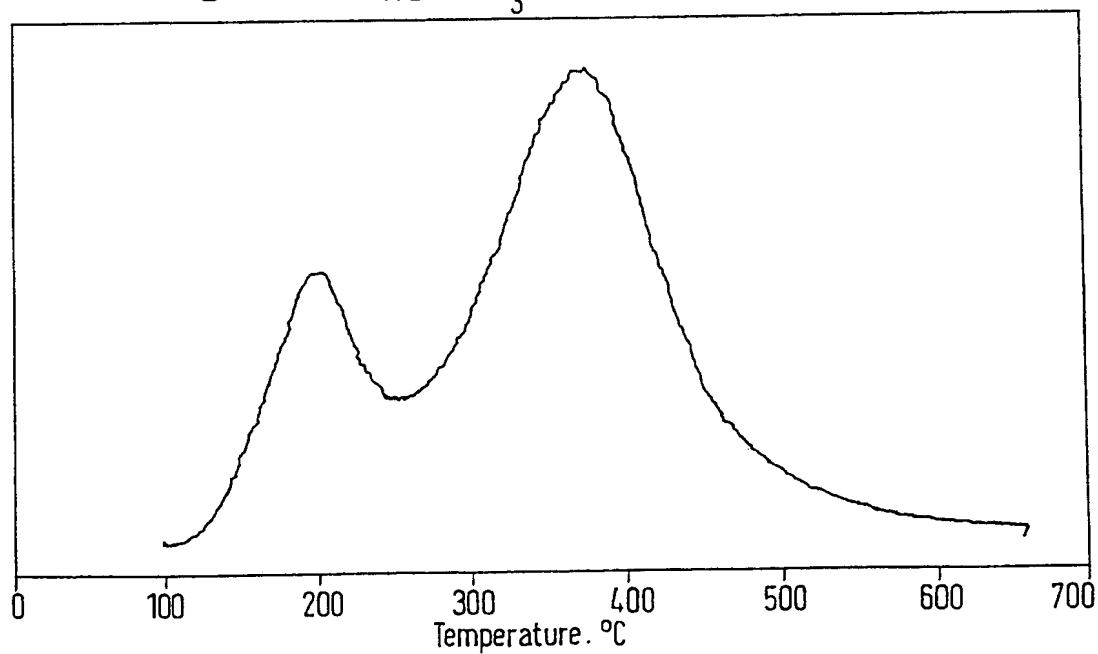
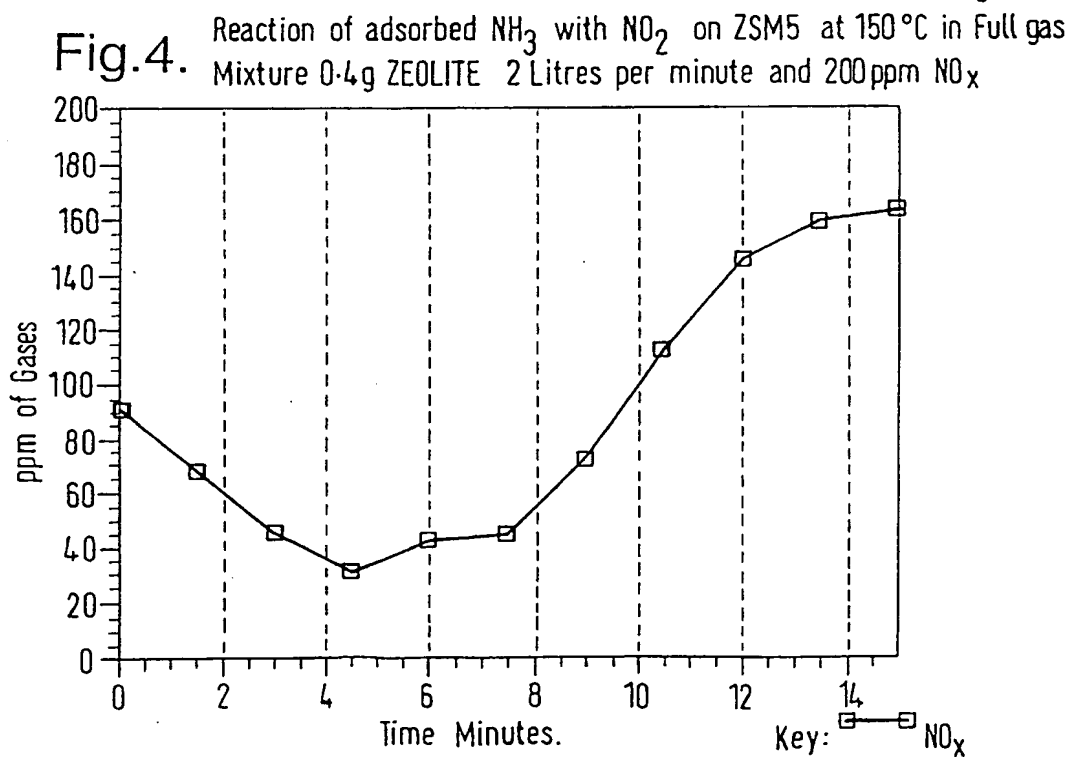
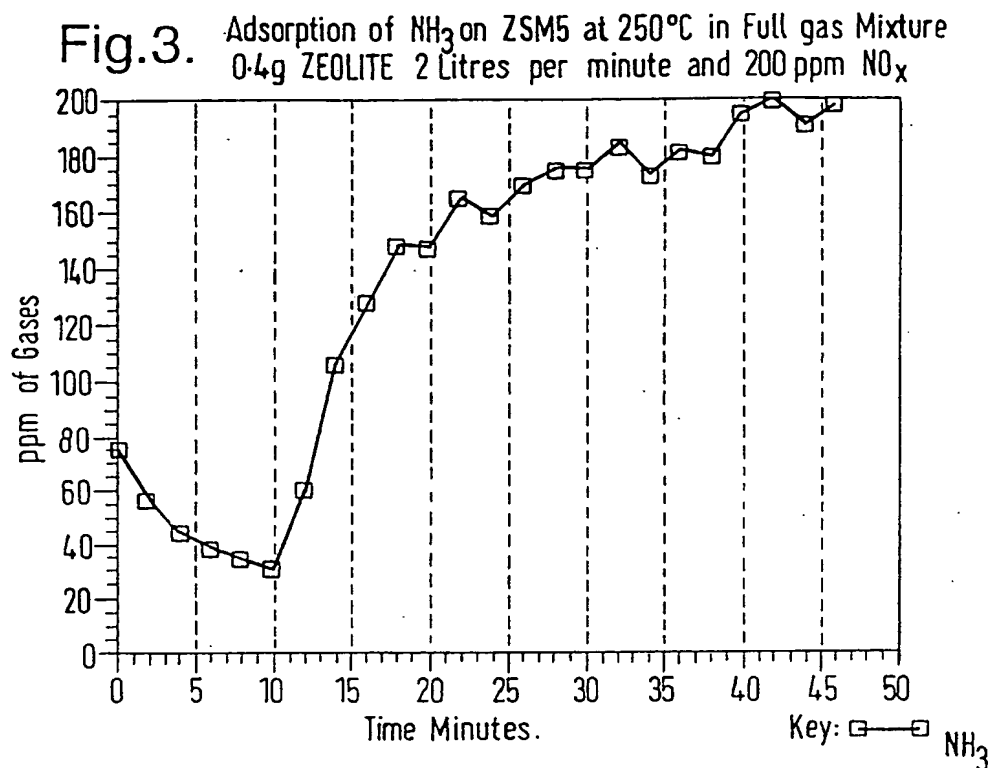
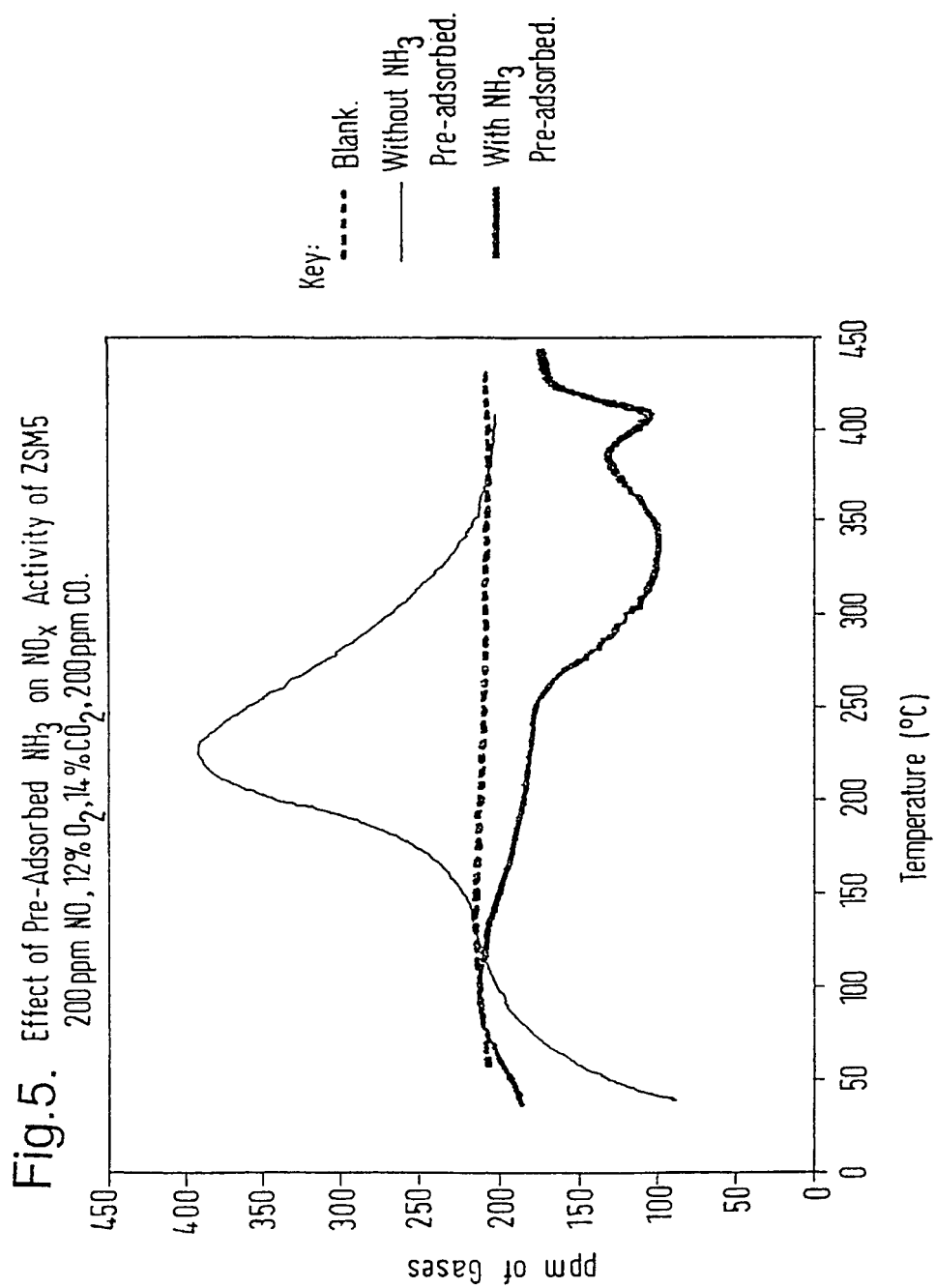


Fig.2. TPD of  $\text{NH}_3$  from ZSM5









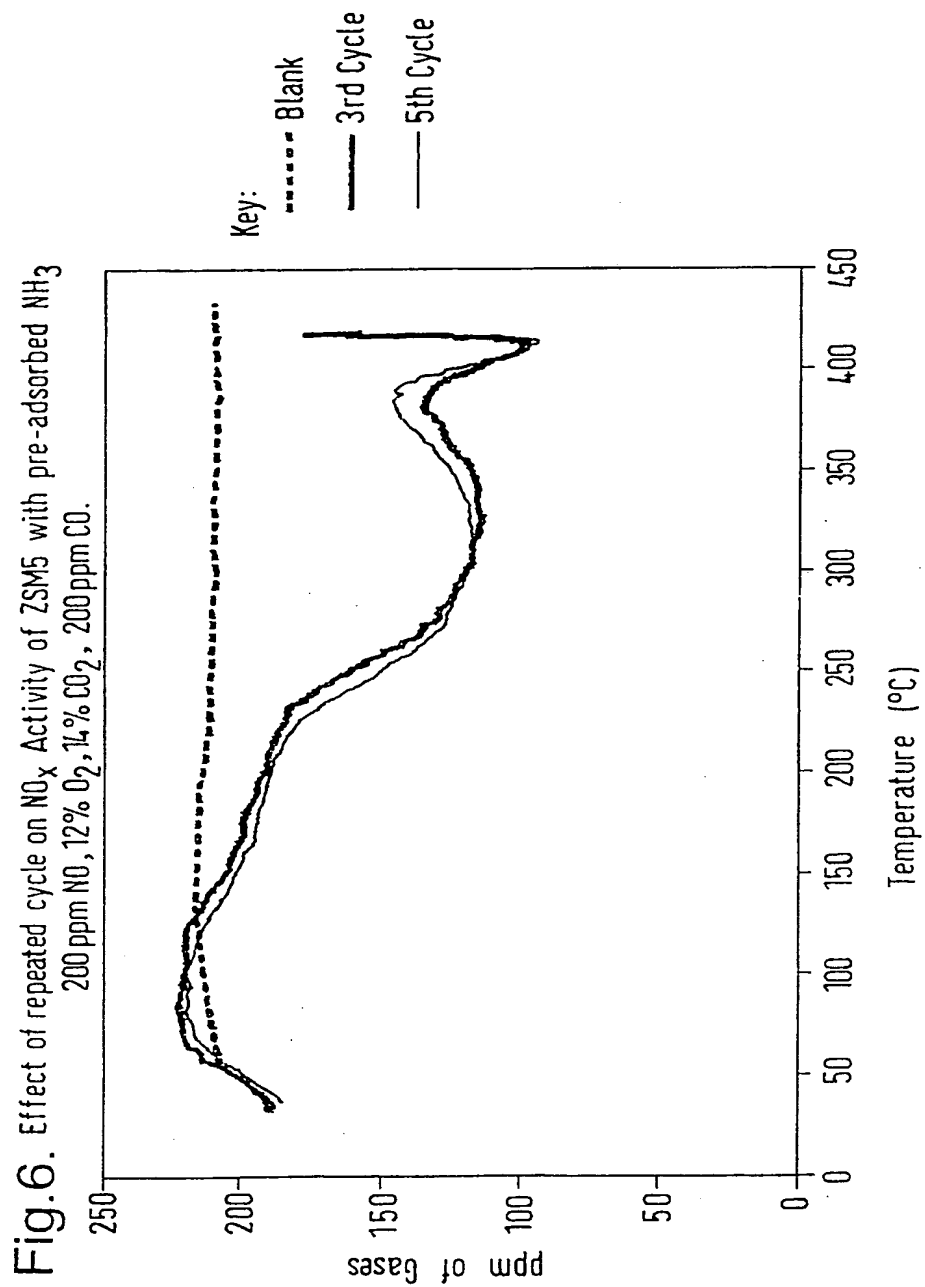
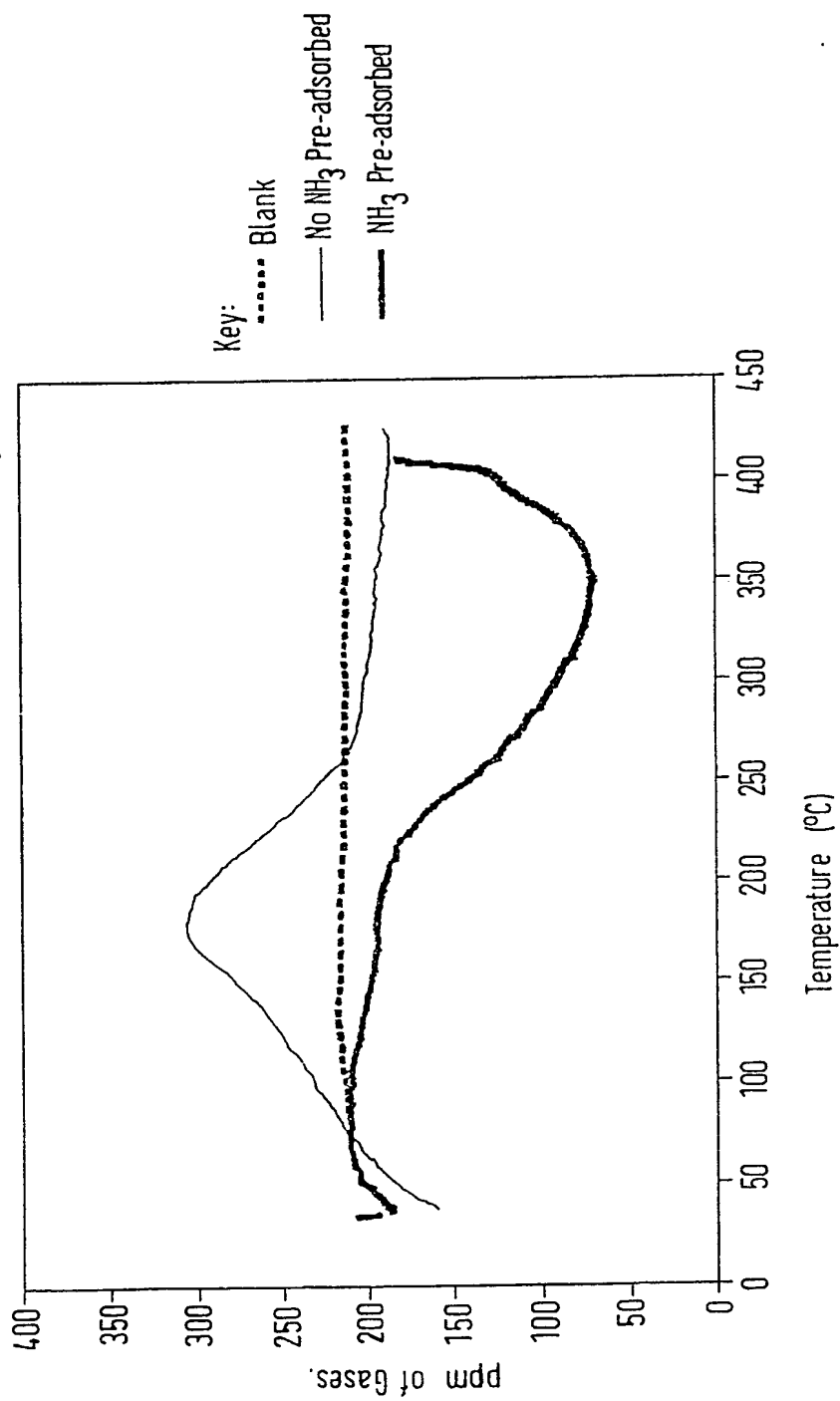
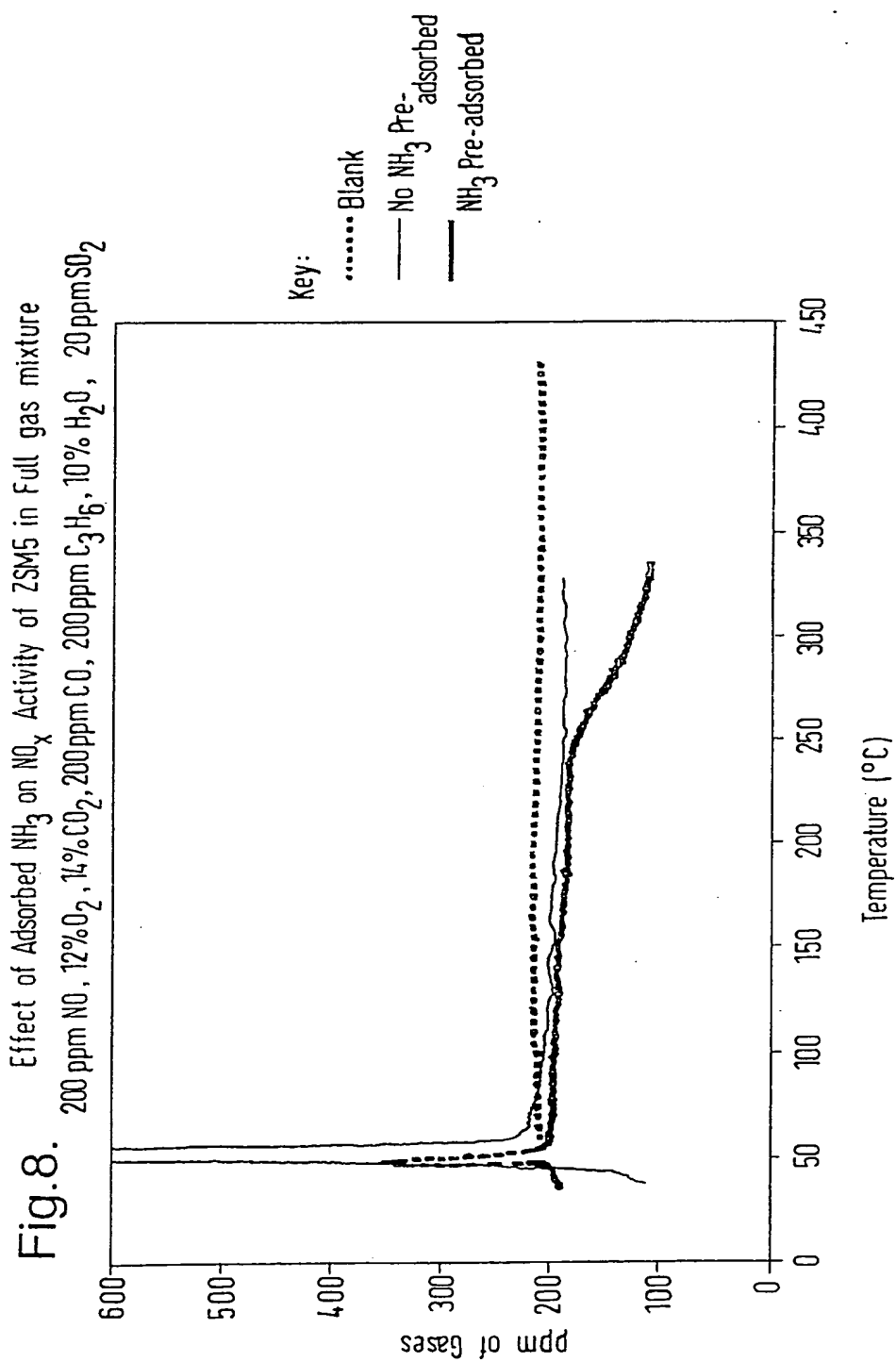
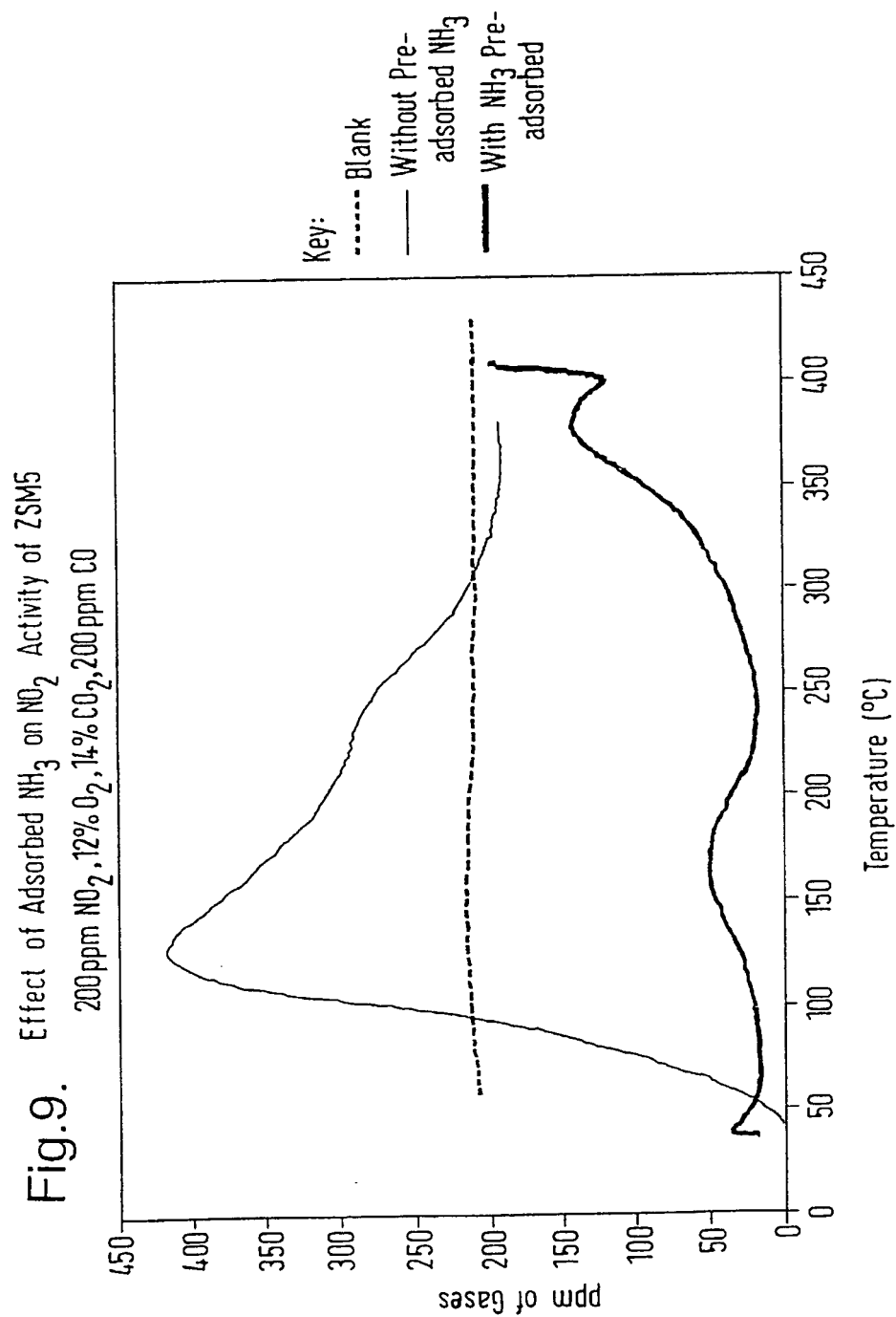
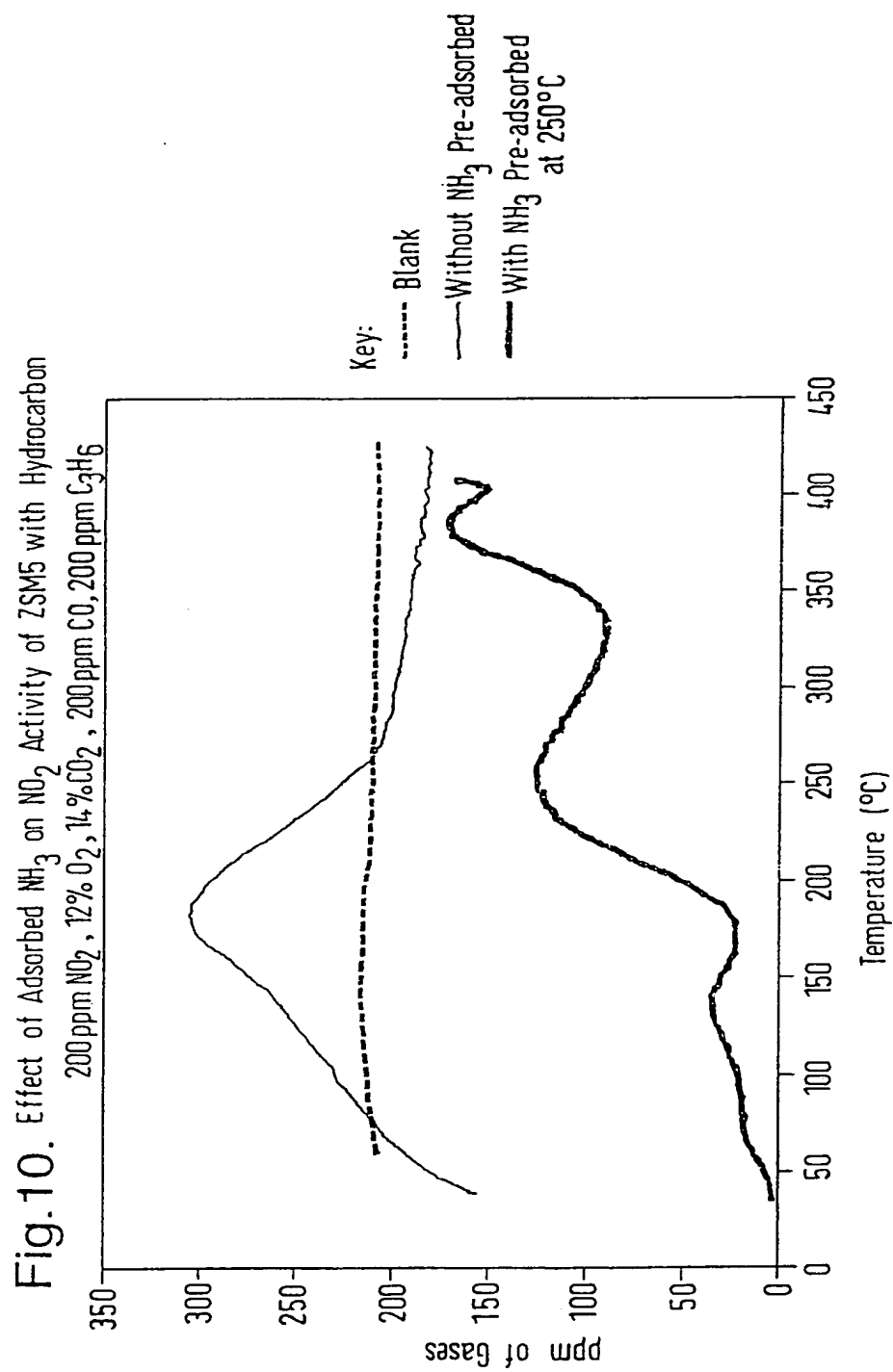


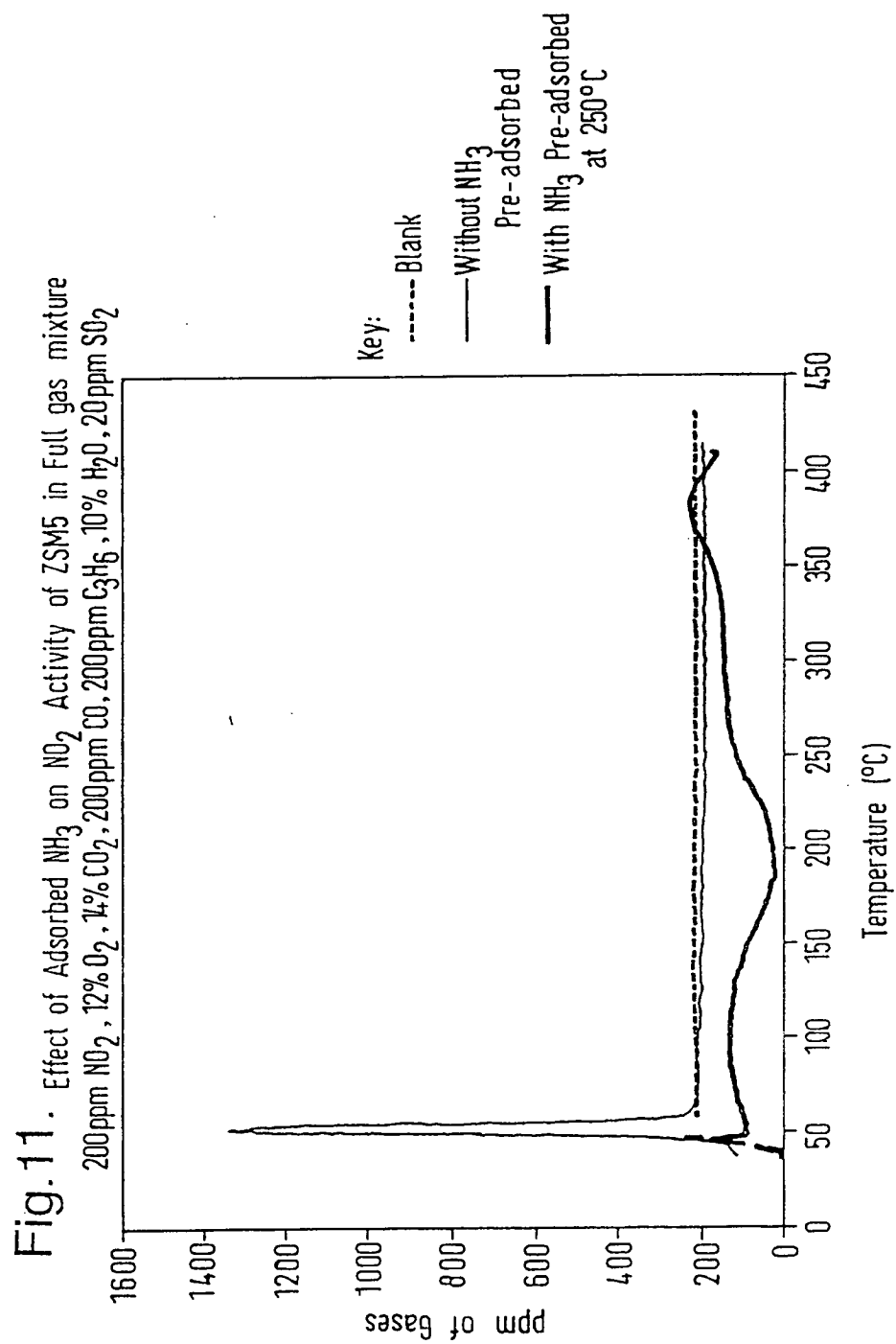
Fig.7. Effect of Adsorbed  $\text{NH}_3$  on  $\text{NO}_x$  Activity of ZSM5 in presence of Hydrocarbon  
200 ppm  $\text{NO}$ , 12%  $\text{O}_2$ , 14%  $\text{CO}_2$ , 200ppm  $\text{CO}$ , 200ppm  $\text{C}_3\text{H}_6$



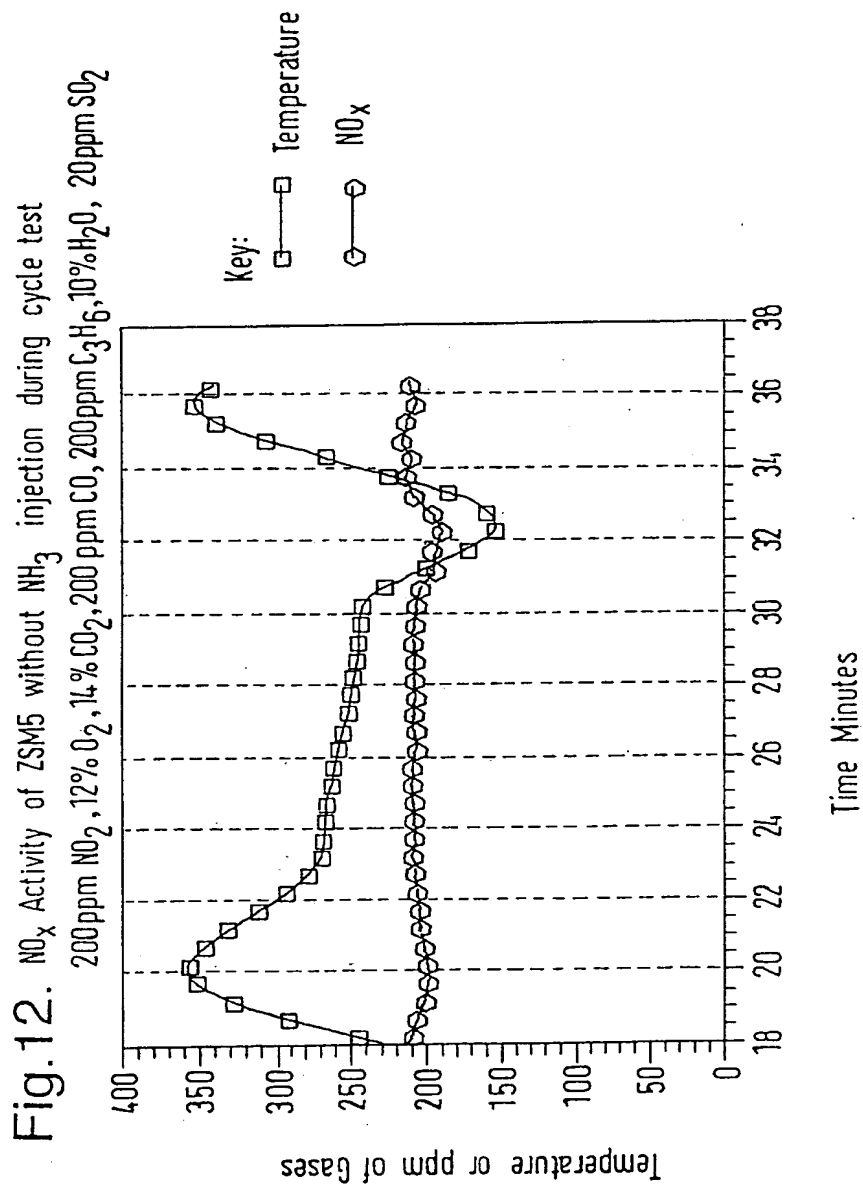












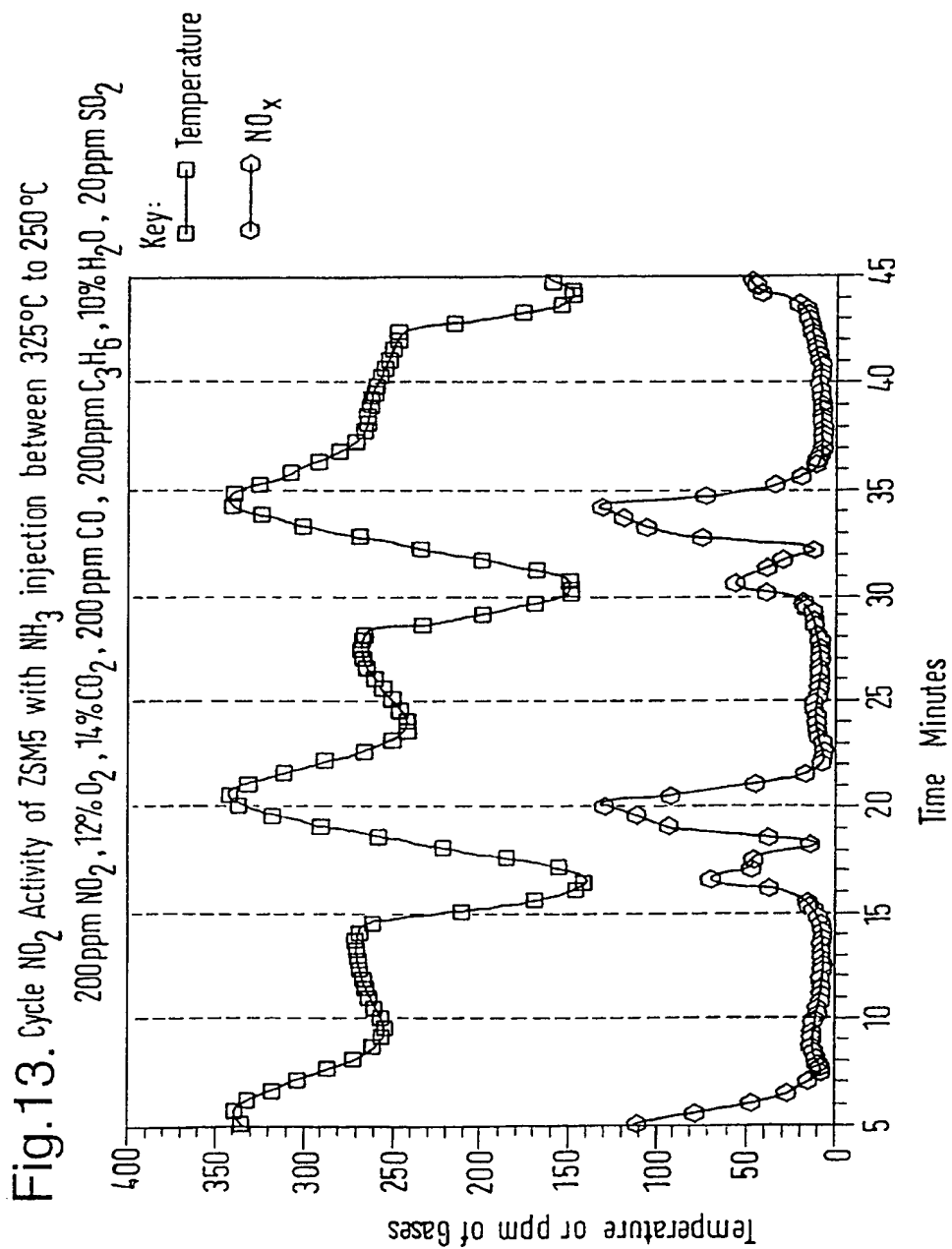


Fig. 14.  
Effect of Adsorbed  $\text{NH}_3$  on  $\text{NO}_x$  Activity of Cu/ZSM5  
200 ppm  $\text{NO}$ , 12%  $\text{O}_2$ , 4%  $\text{CO}_2$ , 200 ppm  $\text{CO}$

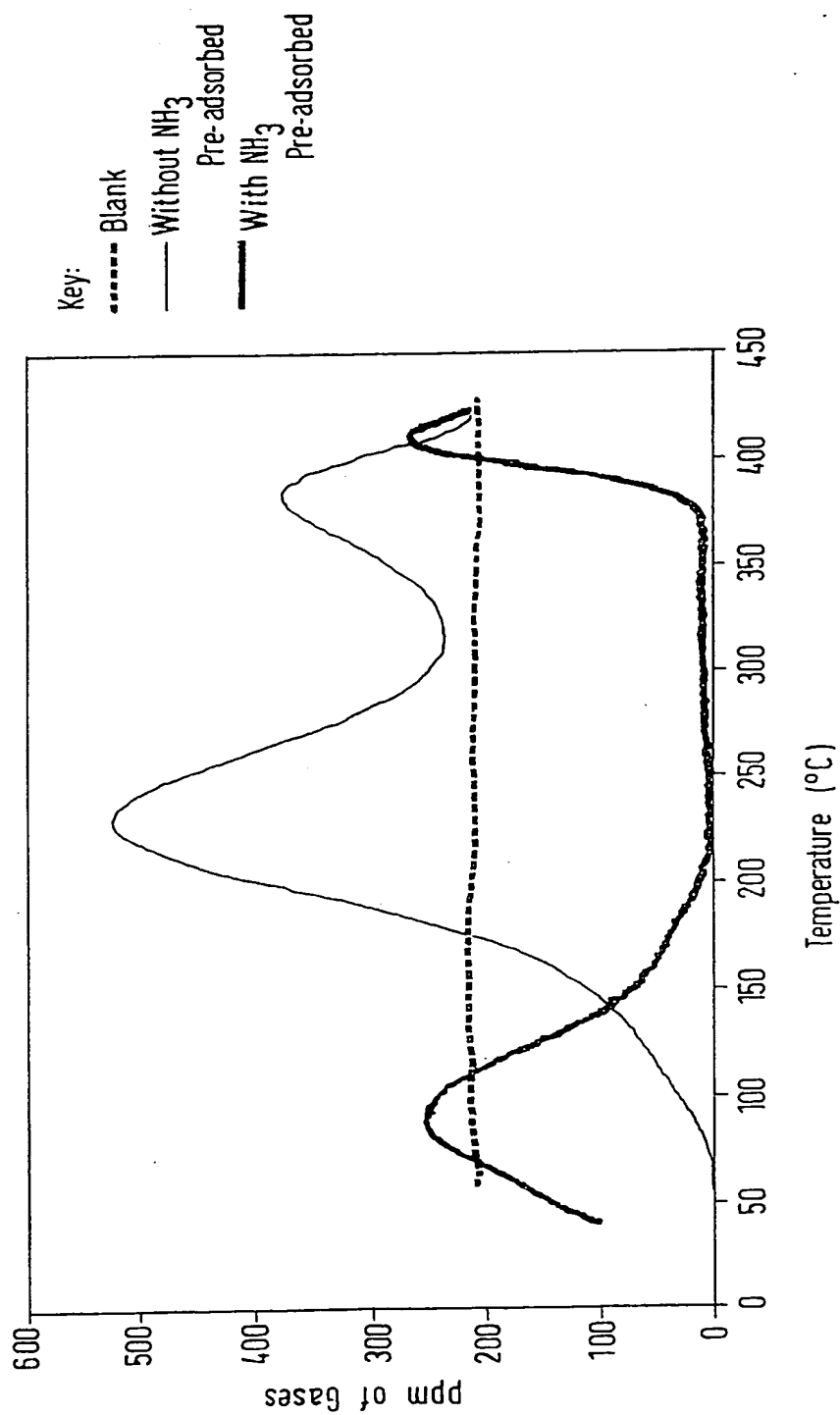
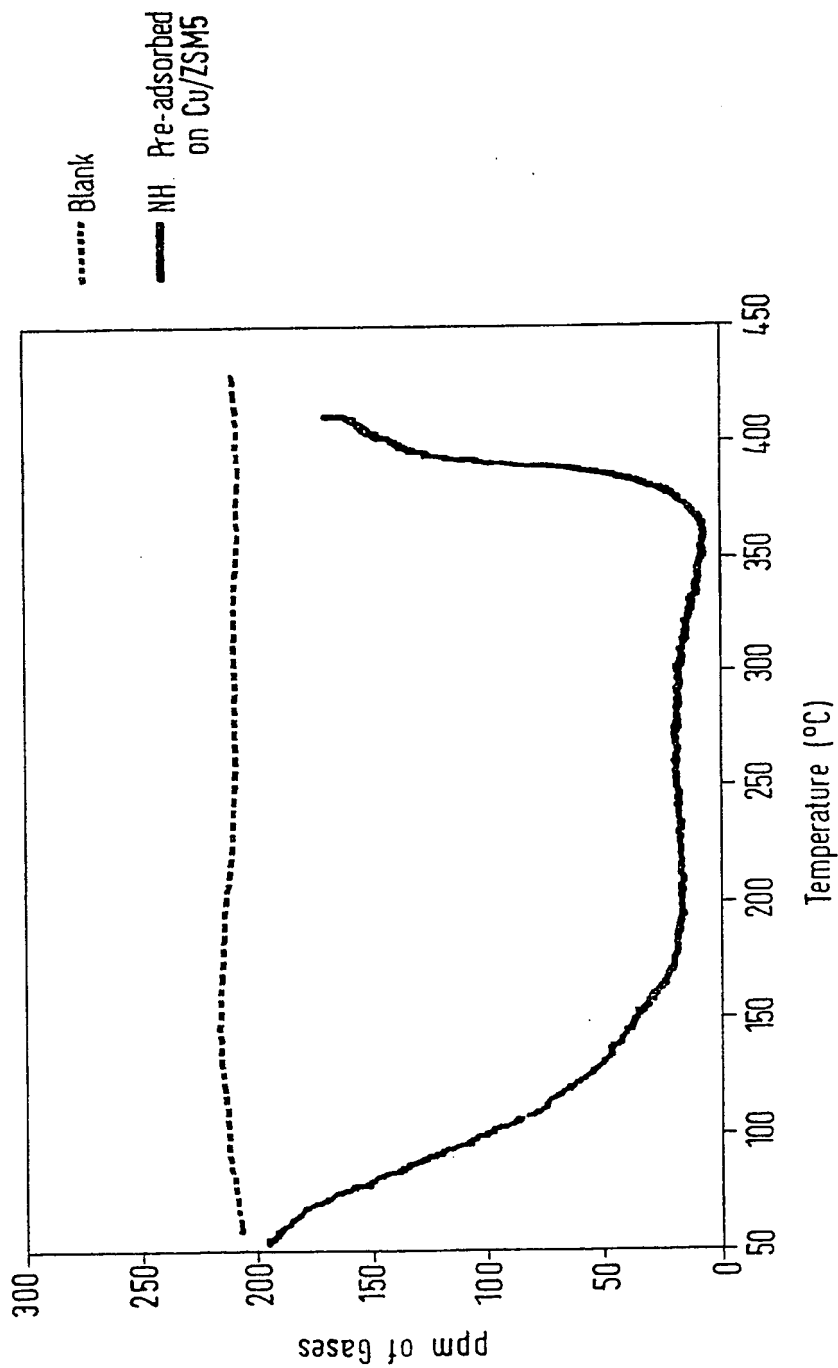


Fig.15. Effect of Adsorbed  $\text{NH}_3$  on  $\text{NO}_x$  Activity of Cu/ZSM5 in Full gas mixture  
200ppm  $\text{NO}$ , 12%  $\text{O}_2$ , 1%  $\text{CO}_2$ , 200ppm  $\text{CO}$ , 200ppm  $\text{C}_3\text{H}_8$ , 10%  $\text{H}_2\text{O}$ , 20ppm  $\text{SO}_2$



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 99/01205

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B01D53/94 B01D53/86 F01N3/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B01D F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 04980 A (HOFMANN LOTHAR ;MATHES WIELAND (DE); NEUFERT RONALD (DE); SIEMENS) 22 February 1996 (1996-02-22) page 2, line 18 - page 3, line 3 page 6, line 13 - page 7, line 2 page 8, line 16-26 ---	1-3,5,11
X	DATABASE WPI Section Ch, Week 9530 Derwent Publications Ltd., London, GB; Class E36, AN 95-227554 XP002111302 & JP 07 136465 A (BABCOCK-HITACHI KK), 30 May 1995 (1995-05-30) abstract --- -/--	1-5,11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

4 August 1999

Date of mailing of the international search report

23/08/1999

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 99/01205

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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